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An approach to the binding state of indium in natural chalcogenides through the analysis of In L_3 edge XANES spectra

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Abstract

A study using synchrotron radiation X-ray absorption spectroscopy at In L_3-edge is presented, as a contribution to interpret the binding state of indium in natural chalcogenides considering the increase of applications of this scarce metal.

Introduction

Discovered in 1863, indium is widely used in various technological fields (e.g. low melting-temperature alloys, solders, electronics) and lately in innovative nanotechnologies to produce "high-tech devices" by means of new materials, namely liquid crystal displays (LCDs), organic light emitting diodes (OLEDs) and the recently introduced transparent flexible thin-films [1] manufactured with ionic amorphous oxide semiconductors (IAOS).

Unlike many scarce metals (e.g., tin), indium does not form specific minerals; it is a chalcophile element that occurs dispersed within polymetallic sulphides and the Iberian Pyrite Belt (IPB) – an important metallogenic province crossing the south of Portugal and Spain – is a promising supplier within Europe [2]. The recovery of indium stands mostly on the zinc extraction from sphalerite, ZnS – the prototype of the so-called "*tetrahedral sulphides*" where the cations fill half of the available tetrahedral sites in a cubic closest packing of sulphur anions. It is still not clear whether In stands preferably in solid solution within ZnS or if it may be concentrated in dispersed exsolved phases [3,4].

Indium consumption is expected to increase in the next years despite its low content in the Earth, thus an X-ray absorption near-edge spectroscopy (XANES) study at In L_3-edge was undertaken with the aim to contribute to the understanding of the indium binding state in natural chalcogenides.

Results

X-ray absorption experiments at In L_3-edge were carried out using the instrumental set-up of ID-21 beamline at the ESRF (European Synchrotron Radiation Facility, in Grenoble/France) and XANES spectra were collected in fluorescence yield mode. Polymetallic chalcogenide ore samples (In ~90 ppm) from Lagoa Salgada [5] were irradiated, along with metallic indium

and various model compounds displaying distinct bonding situations of In to other ligands (oxygen and halides). As an attempt to locate In-rich nanophases, preliminary topochemical mappings of selected fragments from ore samples were performed with the scanning X-ray microscope (SXM).

In L_3-edge XANES spectra display a similar general trend for the model compounds InF_3 and In_2O_3, both containing In^{3+} and for irradiated points in ore samples, displaying two shoulders; an additional weak white-line at 3726.5 eV (bellow the energy of L_3-edge for indium metal, 3730 eV) was noticed in spectra collected from a chalcogenide sample [6].

Comments and conclusions

The presence of a white-line in In L_3-edge XANES spectrum denotes non-occupied electronic states in indium atoms [7]. The closest packing array built up by S^{2-} anions in most sulphide minerals occurring in ore samples - chalcopyrite, sphalerite, tetrahedrite-tennantite, galena - is very suitable to lodge polymetallic cations by filling closely located interstitial sites, so it is not to exclude that interactions may take place between neighbor In cations, thus accounting for details observed in XANES spectra. Further study is in progress to explore this hypothesis.

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